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Temperature Dependence of Photon-Gated Persistent Spectral Hole-Burning  
for the meso-tetra-p-tolyl-Zn-Tetrabenzoporphyrin-Chloroform  
System in poly(Methylmethacrylate)

by

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**TEMPERATURE DEPENDENCE OF  
PHOTON-GATED PERSISTENT SPECTRAL HOLE-BURNING  
FOR THE meso-TETRA-p-TOLYL-Zn-TETRABENZOPORPHYRIN/CHLOROFORM  
SYSTEM IN POLY(METHYLMETHACRYLATE)**

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**ABSTRACT:**

One- and two-color persistent spectral hole-burning properties of the electron donor-acceptor system meso-tetra-p-tolyl-Zn-tetrabenzoporphyrin/chloroform in poly(methylmethacrylate) are examined *versus* temperature from 1.5 to 90 K. The efficiency for photon-gated (two-color) hole-burning is independent of temperature, while the one-color hole-burning efficiency decreases as the temperature is raised from 1.5 K. Raising the temperature improves the gating ratio (ratio of two- to one-color hole-burning efficiencies) from  $10^2$  at 1.5 K to  $10^4$  at 90 K. The low-power, short-burn-time hole width is also measured from 1.5 K to 90 K and is found to have a  $T^{2.17 \pm 0.07}$  power law behavior.

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## I. Introduction

Persistent spectral hole-burning has been utilized as both a tool for studying relaxation processes in amorphous solids<sup>1</sup> and as a means for possibly achieving high-density frequency-domain optical storage<sup>2</sup>. Persistent spectral holes are formed in inhomogeneously broadened absorption lines when a photoinduced change occurs in the subset of absorbers that are in resonance with a narrowband laser beam. If the photoreacted centers do not absorb at the original wavelength, a dip in absorption or spectral "hole" is formed that may be detected by subsequent measurement of the absorption line.

While a number of recent investigations have focused upon the process of hole formation at liquid nitrogen temperatures<sup>3,4</sup>, others have considered photon-gated mechanisms in light of the limitations of single-photon, monophotonic reactions with no threshold<sup>5</sup>. In photon-gated hole-burning, two photons (ideally of different wavelengths) are required to induce the photochemical reaction leading to hole formation. In effect, the first photon produces the site-selection and the second photon acts as a "gate" on the photochemistry. Both inorganic<sup>6</sup> and organic<sup>7</sup> examples of photon-gating have been found, and the number of such systems continues to increase<sup>8,9</sup>.

Recently, the characteristics of and mechanism for a particularly high-efficiency photon-gated material undergoing donor-acceptor electron transfer were reported at the fixed temperature of 1.5 K<sup>10</sup>. The material is composed of meso-tetra-p-tolyl-Zn-tetrabenzoporphyrin (TZT) or its Mg analog combined with various halomethane acceptors in PMMA (poly(methylmethacrylate)). The efficiency of this photoreaction was shown to be sufficiently high that detectable holes could be formed in 30 ns with focused light from a 10 mW continuous-wave red laser, followed by a longer gating pulse in the green<sup>11</sup>.

This paper reports the temperature dependence of the photon-gating properties of one material in this donor-acceptor class, TZT/ $\text{CHCl}_3$ /PMMA, from 1.5 to 90 K. Surprisingly, the ratio of the two-color efficiency to the one-color efficiency increases with temperature, and this effect is shown to be due to a dramatic decrease in one-color hole formation, which is a photophysical process. Since the hole width controls the peak absorption cross section (a crucial quantity reflecting the ability of the light to excite each molecule), the temperature dependence of the hole width is also presented.

## II. Experimental Details

Samples of TZT/PMMA/ $\text{CHCl}_3$  were prepared in a manner similar to that utilized previously<sup>10</sup> Solutions of (0.5 g PMMA)/(5 ml  $\text{CHCl}_3$ ) were prepared by dissolving high purity monodisperse PMMA in  $\text{CHCl}_3$ . The polymer material with  $M_p = 107,000$  and  $M_w/M_n = 1.1$  was obtained from Polymer Laboratories. A small quantity of the TZT dopant (synthesized by V. Y. Lee of our laboratory) was added to the PMMA/ $\text{CHCl}_3$  solution under yellow and red lights, and all subsequent sample handling was performed under yellow and red lights. Samples were made by placing a few drops of the TZT/ $\text{CHCl}_3$ /PMMA solution on glass cover slips and allowing the chloroform to evaporate in air at room temperature for several minutes before insertion into a cold optical immersion cryostat to freeze in the remaining solvent. Every attempt was made to make the samples similar to one another; however, the exact concentration of the acceptor chloroform could not be easily controlled. The samples were mounted over a 4 mm aperture on a sample wand and a calibrated resistance thermometer was pressed into the soft PMMA immediately adjacent to the aperture. Sample thickness varied from 80 to 200  $\mu\text{m}$ .

The temperature dependence of the hole-burning efficiencies and the hole widths was examined from 1.5 K to 90 K. For temperatures between 1.5 and 2.1 K, the sample was immersed in superfluid He and the temperature was controlled by throttling the He gas

pumping rate. Above 4.2 K, the sample temperature was controlled by warming the He gas before it entered the sample chamber. During hole-burning, the largest rise in sample temperature occurred near 5 K and was no more than 0.15 K.

The optical arrangement for burning persistent spectral holes is also similar to that previously utilized<sup>10</sup>. In order to burn one-color persistent spectral holes, an Ar<sup>+</sup>-laser-pumped single-frequency Rhodamine B dye laser (linewidth 3 MHz) was used to excite the TZT transition at wavelengths between 624.7 and 630.0 nm, with wavelengths determined by a Burleigh wavemeter. The peak of the TZT/CHCl<sub>3</sub>/PMMA (0-0) S<sub>1</sub> ← S<sub>0</sub> transition is near 624.7 nm. Sample optical densities at the laser burn frequency were between 1.0 and 0.15. The dye laser intensity during writing was varied between 10<sup>-6</sup> and 4 × 10<sup>-2</sup> W/cm<sup>2</sup> with fixed neutral density and variable attenuators. Gated (two-color) persistent spectral holes were burned in the TZT S<sub>1</sub> ← S<sub>0</sub> origin band by simultaneously exposing the sample to the dye laser and 514.5 nm Ar<sup>+</sup> ion laser light. The optical density of the samples at the gating wavelength was less than 0.04 (e.g. see Ref. 10, Fig. 3). This small amount of absorption (in the singlet states) at the gating wavelength leads to a small amount of broadband bleaching of the S<sub>1</sub> ← S<sub>0</sub> inhomogeneous line. The Ar<sup>+</sup> ion laser gating intensity was held fixed at 0.5 W/cm<sup>2</sup> throughout. Repeatable sample exposures to the laser beams were obtained with electronically controlled shutters.

Holes burned with the laser were detected in transmission using two methods. Below 6 K, the hole widths were narrower than the 20 GHz single-frequency tuning range of the dye laser and were measured by repetitively tuning the laser frequency and detecting the transmitted laser intensity using a precision ratiometer<sup>10</sup>. Above 6 K, another method was employed to measure the consequently broader holes. A third probe beam from a grating spectrometer was overlapped with the hole-burned sample volume. The spectrometer consisted of a 75 W tungsten lamp which was low-pass filtered, polarized, and dispersed in a 3/4 m monochromator. The dispersed probe light was then directed through the sample

and detected with an RCA C31034A-02 GaAs photomultiplier tube. The phototube current was measured with an electrometer with a 1 second time constant. The spectrometer resolution was determined to be 15 GHz by scanning the monochromator through the dye laser line. The spectrometer light intensity incident on the sample never exceeded  $10^{-6}$  W/cm<sup>2</sup>.

### III. Experimental Results

Figure 1 shows examples of one- and two-color hole-burning near the peak of the singlet-singlet origin for TZT/CHCl<sub>3</sub>/PMMA at 1.55 K. The two-color hole in Fig. 1(a) was burned by simultaneous exposure for 2 seconds to a weak write beam near 625.223 nm and a stronger gating beam at 514.5 nm. Without the gating beam, a one-color hole of the same depth as the 2.0 s two-color hole at 1.55 K requires a 200 second burn time, as in Fig. 1(c) (hole on the left). The one- and two-color holes both slightly broaden on a one hour time scale (Fig. 1(a)-(f)), but the hole areas decay differently.

The different behavior of the one- and two-color hole areas in Fig. 1 is plotted in Figure 2 on a log(time) axis. The two-color hole area (Fig. 2(a)) remains essentially constant, but the one-color hole area decreases logarithmically for this range of decay times (50 to  $5 \times 10^3$  s). The constant area of the two-color hole is consistent with a photochemical hole-burning mechanism with no back-reaction and the decaying one-color hole is consistent with a photophysical hole-burning mechanism<sup>12</sup> (see Sec. IV).

When the temperature is raised above 1.55 K, the ability to burn one-color holes decreases relative to the ability to burn two-color holes. Figure 3 shows one- and two-color holes burned at 20 K into the TZT/CHCl<sub>3</sub>/PMMA origin band. The two-color hole in Fig. 3(a) was burned in 2.0 s, but the one-color hole in Fig. 3(b) required 4380 s to achieve a fraction of the two-color hole depth. The two-color hole area is constant in time before and

after the one-color burn, but decreases during the one-color burn. Notice that the amount by which the two-color hole area decreases is larger than would be expected if the one-color hole area were spread over the inhomogeneous line. This is an example of laser-induced hole-filling (LIHF), a phenomenon recognized by Small et. al. for photophysical holes<sup>13</sup>. The LIHF observed here for a photochemical hole currently lacks a satisfactory explanation.

In order to compare the ability of the TZT/CHCl<sub>3</sub>/PMMA material to form one- and two-color holes at different temperatures, it is more appropriate to compare the quantum efficiencies for hole-burning than the hole depths or burn times. When all defects have the same quantum efficiency, the quantum efficiency for hole-burning may be written

$$\eta = \frac{\left( \frac{1}{T} \frac{dT}{dt} \right) |_{t=0}}{(\sigma I / h\nu)(1 - T_0 - R)} \quad (1)$$

where the initial fractional rate of change of transmission  $(1/T)dT/dt$  can be obtained from a growth curve for the hole,  $I$  is the intensity,  $h\nu$  is the photon energy,  $T_0$  is the initial transmission, and  $R$  is the reflection loss. This efficiency is the inverse of the mean number of write beam photons absorbed per hole-burned TZT molecule. Since for an amorphous host there is probably a distribution of efficiencies,  $\eta$  should be viewed as an apparent or effective efficiency for comparison purposes. The zero-phonon line peak cross section  $\sigma$  is proportional to the inverse of the hole width in the low power, low burn-fluence limit. As a measure of the temperature dependence of the quantum efficiency for hole burning, we define an unnormalized efficiency  $\eta^*$ , which is proportional to the actual quantum efficiency  $\eta$  (at least for one-color holes) as

$$\eta^* = \frac{\Lambda \tilde{\nu}_H \left( \frac{1}{T} \frac{dT}{dt} \right) |_{t=0}}{P_i (1 - T_0 - R)} \quad (2)$$

where  $P_1$  is the ( $\lambda_1$ ) write beam power (for fixed spot size) and  $\Delta\tilde{\nu}_H$  is the persistent spectral hole width (full-width at half-maximum). Since the gating beam intensity is held constant at the near-optimal value of 0.5 W/cm<sup>2</sup> throughout these experiments, we use the  $\eta^*$  expression for both one- and two-color hole-burning. In the case of two-color hole-burning, it is clear that  $\eta^*$  represents an overall measure of the efficiency of hole production, rather than any particular microscopic quantum efficiency.

Figure 4 shows the growth of one- and two-color hole depths and widths at 2.03 and 16.2 K with burning time. In Figs. 4(a) and 4(b), the initial slopes of the one- and two-color hole growth curves at 2.03 K differ by a factor of 100 (compare the time axes). Since the 2.03 K hole widths and write beam intensities in Figs. 4(a) and 4(b) are nearly the same, the one- and two-color  $\eta^*$  values at 2.03 K also differ by a factor of approximately 100, as shown earlier in Fig. 6 of Ref. 10.

The effect of raising the temperature on the two-color growth rate and hole width is seen in Figs. 4(b) and 4(c) -- raising the temperature from 2 to 16 K decreases the two-color hole growth rate by a factor of 15 and increases the hole width by a factor of 50. Since the write beam intensity used to burn the hole in Fig. 4(c) is twice that in Fig. 4(b), the ratio of the two-color  $\eta^*$  values at 16 and 2 K is  $50/(15 \times 2) = 1.7$ . Factor of two error bars are common in measurements of hole-burning quantum efficiencies<sup>14</sup>, so one may conclude that the two-color  $\eta^*$  has not changed significantly with temperature. Note that the two-color hole depth grows more slowly at higher temperatures mostly because the number of TZT molecules with absorption frequencies within one homogeneous width of the write beam frequency has increased and more defects need to be burned to achieve the same hole depth in a given time.

In contrast to the modest factor of 15 decrease in two-color hole growth rate from 2 to 16 K, the one-color hole growth rate decreases much more strongly (compare Figs. 4(a) and 4(d) with 4(b) and 4(c)). It is much more difficult to burn one-color holes at higher



temperatures, so the 16 K one-color hole growth curve shown in Fig. 4(d) required 200 times the intensity as that used in Fig. 4(a); even with this increased intensity the growth rate is still 200 times smaller. initial slope. Hence, in raising the temperature from 2 to 16 K, the one-color  $\eta^*$  value has decreased by  $50/(200 \times 200) = 1/800$ . In other words, while the two-color hole-burning efficiency remains constant, the one-color hole burning efficiency appears to dramatically decrease with temperature.

With such large differences between one- and two-color efficiencies, raising the write beam intensity to burn one-color holes is necessary in order to form one-color holes in a reasonable amount of time. Another reason we found it desirable to raise the write beam intensity has to do with the the small amount of bleaching by the gate alone. Note the small offset in the transmission baseline from a value of 1.0 in Fig. 1(a). This broadband bleaching occurs due to the small amount (less than 10 %) of absorption by the vibronic tails of the  $S_1 \leftarrow S_0$  transition at the 514 nm gating beam wavelength. The amount of broadband bleaching by the gating light is temperature independent and only depends on the gating light exposure time. Since at constant write intensity the two-color burn times become longer with temperature, the amount of overall line bleaching per two-color burn becomes greater. Raising the write beam intensity as the temperature is raised then allows for short, constant two-color burn times on the order of 2.0 seconds and a tolerably small amount of bleaching by the gating light.

One possible adverse effect of increasing the write beam intensity can be seen by comparing the hole widths in Figs. 4(c) and 4(d). Namely, increasing the write beam intensity can power broaden the hole, which masks the low-power hole width. Since we wish to raise the write beam intensity with temperature without power broadening the hole widths, the effect of power broadening was examined with temperature.

Figure 5 shows how two-color hole widths power broaden at several temperatures. To acquire this data, at a fixed temperature a write beam burn fluence was selected which yields

shallow holes ( $(\Delta\alpha)/\alpha = 0.05$  to  $0.1$ ). The hole width was then measured as a function of the burn intensity at constant burn fluence (this avoids the additional broadening that accompanies photochemical hole depth saturation<sup>15</sup> at high burn fluence). At low intensities, the hole width changes little. As the intensity is raised further, the hole width is observed to broaden. The onset of power broadening occurs at higher intensities as the temperature is raised (Fig. 5(a)-(d)). The expression for the hole width as a function of intensity due to power broadening is

$$\Delta\tilde{\nu}_{H} = \frac{\Delta\tilde{\nu}_{H}^0}{2} (1 + \sqrt{1 + I/I_{\text{sat}}}), \quad (3)$$

where  $I_{\text{sat}}$  is the (three-level) saturation intensity which is proportional to a product of the dephasing rate, excited state decay rate, and the ratio of the leaving and entering rates for the intermediate state<sup>15</sup>. The low-power limiting hole width  $\Delta\tilde{\nu}_{H}^0$  is only proportional to the dephasing rate. The power broadening expression (Eqn. 3) was fit to the data to find the saturation intensities at various temperatures (see the Fig. 5 caption). The saturation intensity increases with the hole width, but not simply in proportion to the hole width. Normally the excited state lifetime, triplet yield, and triplet lifetime are only weakly dependent on temperature; which of these parameters is changing in our case cannot be determined from our data. Nevertheless, knowledge of the rate of hole broadening with intensity allows careful choice of laser intensities for hole width measurements.

Having thus established the upper burn fluence and intensity limits below which there is negligible hole broadening, the low power, short burn-time hole width were measured as a function of temperature. Figure 6 shows the variation of the TZT-CHCl<sub>3</sub>/PMMA  $S_1 \rightarrow S_0$  zero-phonon hole width over two decades in temperature. Relative to the inhomogeneous line width of  $300 \text{ cm}^{-1}$ , the hole widths span a range of  $0.045 \text{ cm}^{-1}$  to  $100 \text{ cm}^{-1}$  over 1.5 to 90 K. The data can be fit with a power law expression of the form

$$\Delta\tilde{\nu}_{H}^0 = \Delta\tilde{\nu}_{H}^0(T=0) + \beta T^n, \quad (4)$$

where the low temperature limiting hole width is  $0.035 \pm 0.006 \text{ cm}^{-1}$ , the coefficient  $\beta$  is  $0.006 \pm 0.001 \text{ cm}^{-1}/\text{K}^{2.17}$  and the power law exponent is  $n = 2.17 \pm 0.07$ .

The final experimental result to be presented in this paper is of importance to possible frequency-domain optical storage applications. For the purposes of this paper, we define the ratio of two- and one-color  $\eta^*$  values to be the gating ratio. The gating ratio should be made as high as possible in order to maximize the nondestructive reading of a persistent hole. The temperature dependence of the two- and one-color  $\eta^*$  values is presented in Fig. 7. The two-color  $\eta^*$  (Fig. 7(a)) is essentially independent of temperature from 1.5 to 90 K. In contrast, the one-color  $\eta^*$  decreases substantially as the temperature is raised from 1.5 K to 90 K. (The straight line fits in Fig. 7 are guides to the eye.) By inspection of Fig. 7, one sees that the gating ratio is improved from  $\approx 10^2$  to  $10^4$  as the temperature is raised from 1.5 K to 90 K. The large scatter in the data is due mostly to sample to sample variations in the acceptor concentration<sup>16</sup>. Another possible source of error in the one-color data that was not examined is the possibility that at higher temperatures (where higher one-color intensities were used), a fraction of the one-color hole may actually be a self-gated photochemical hole. This would mean that the actual one-color photophysical efficiency would decrease even faster than that shown in Fig. 7(b).

#### IV. Discussion

Two results are discussed in this section: (A) the one-color photophysical hole-burning efficiency decrease with temperature in Fig. 7, and (B) the approximately  $T^2$  dependence for the hole width over a temperature range of 1.5 K to 90 K in Fig. 6. The temperature dependence of the one-color hole burning efficiency is discussed in terms of current models for photophysical hole burning in glasses. The  $T^2$  hole width temperature dependence is compared with results previously found for inorganic and organic glasses.

### *A. The apparent hole-burning efficiency temperature dependence*

The mechanism for photophysical hole-burning in amorphous solids has been explained in terms of changes in the structure of the host material during an optical cycle of the defect or guest molecule<sup>13,17</sup>. The structural changes are thought to occur through tunneling transitions of as-yet-unidentified tunneling systems known as two-level systems (TLS). The TLS have a wide distribution of tunneling rates, which give rise to relaxation behavior that is logarithmic on time scales intermediate between the maximum and minimum relaxation times in the glass<sup>12</sup> (see Fig. 2(b)). The hole-burning mechanism has been described as either (a) a phonon-assisted tunneling (PAT) transition occurring after a guest molecule has been excited into an electronic excited state by the laser<sup>18</sup>, or (b) as a simultaneous electronic-TLS transition<sup>13</sup>. In case (a), the efficiency for hole-burning is given by the rate of PAT in the electronic excited state relative to the rate of decay out of the excited state. In the latter case (b), the hole-burning efficiency depends on the strength of the coupling of the guest molecule to the TLS. For either of the proposed mechanisms, there is probably a wide distribution of hole-burning efficiencies because of the wide distribution of tunneling rates or coupling strengths. Centers with high efficiency are burned first, so the initial growth of a photophysical hole and our definition of the measured  $\eta^*$  involves high efficiency centers. After a center is burned, the center must have reasonably large barriers to relaxation of the TLS in the ground state in order to contribute to the persistent hole. Hence, centers that contribute to the initial growth of a (persistent) hole are the small fraction of centers that have both high burning efficiency and long ground state relaxation times compared to the burning and detection time scale.

In Fig. 7, the photophysical one-color  $\eta^*$  is observed to decrease with temperature, which means that the number of high efficiency defects contributing to the hole within the burn time or remaining burned until the hole is detected decreases. For mechanism (a), PAT increases with temperature as the phonon occupation numbers increase, and in individual

center's efficiency for hole-burning should also increase. For mechanism (b), the coupling strength and associated crossing transitions are not expected to be temperature dependent, and the efficiency for photophysical hole-burning should be temperature independent. The decrease in  $\eta^*$  must then be due to an increase in the ground state relaxation rates either by PAT or thermally activated jumping over ground state barriers. In other words, the measured efficiency for production of persistent holes decreases with temperature apparently because the fraction of high efficiency defects that do not undergo ground state relaxation within the hole-burning time and before hole detection decreases. It is hoped that by presentation of these results, more detailed theoretical explanations of this phenomenon will be generated.

### ***B. Two-color hole width temperature dependence***

The two-color, low-power hole width temperature dependence for TZT in the organic polymer PMMA with excess  $\text{CHCl}_3$  is fit nicely with a  $T^2$  power law from 1.5 K to 90 K. Recent reviews of homogeneous linewidth broadening with temperature in glasses have pointed out that the temperature range studied for inorganic glasses (0.05 to 800 K) spans a much broader range than for organic glasses (0.05 to 25 K) (see Table 1 of Ref. 19 and Table 2 of Ref. 20). For homogeneous linewidth studies in inorganic glasses above 10 K, the temperature exponent is typically 2. A  $T^2$  dependence for the dephasing rate is attributed to a two-phonon Raman scattering process. In crystals, the two-phonon scattering process gives rise to a  $T^2$  dephasing rate above the Debye temperature, which is on the order of 100 K. The  $T^2$  dependence in glasses down to 10 K has been ascribed to an effective lowering of the Debye temperature by the large density of TLS states at low frequencies<sup>21</sup>.

In studies of homogeneous linewidths in organic glasses where data is obtained only below 10 K or 20 K, the temperature exponent is found to be between 1 and 2 in many cases

<sup>20</sup> with a large number of values <sup>22</sup> near 1.3. The lower exponents are associated with dephasing by the large density of low frequency TLS states.

We have extended the range of temperature over which the homogeneous holewidth has been studied with a single technique for an organic glass from below 10 K to well above 10 K, and find that a  $T^2$  dependence fits the data in both regions (see Fig. 6). The  $T^2$  behavior in the region above 10 K is similar to that found for inorganic glasses. However, for many organic glasses below 10 K, exponents below 2 are found, and the theoretical models can generate a range of temperature exponents <sup>23</sup>. What is useful about the present measurement is the large temperature range over which the low-power limiting hole width can be measured for an organic glass.

A note about the scatter in our measured hole widths below 10 K is in order. In our samples, the local environment around the TZT molecules by necessity consists of PMMA host chains and a large number of chloroform acceptor molecules. The effect of residual solvent on homogeneous line width temperature dependence in the low temperature region ( $T < 5$  K) for organic glasses has been examined <sup>24</sup>. Residual solvent can raise the low temperature limiting linewidth without changing the  $T < 5$  K exponent. Since special precautions were not taken to absolutely control the amount of  $\text{CHCl}_3$  solvent in the TZT/ $\text{CHCl}_3$ /PMMA samples, varying amounts of solvent from sample to sample may be responsible for the larger scatter in the low temperature data of Fig. 6.

The low temperature limiting hole width of  $0.035 \text{ cm}^{-1}$  is much larger than the  $0.0005 \text{ cm}^{-1}$  width expected from the fluorescence decay time alone <sup>25</sup>. One possible explanation for this result could be spectral diffusion effects; recent careful comparisons between widths measured by hole-burning and widths measured by photon echoes have illustrated the importance of such effects in amorphous hosts <sup>26</sup>. For this reason, we held the detection time fixed (at several minutes) for our measurements whenever possible. Clearly, the present system with its controllable two-color hole-burning mechanism and photophysical one-color

mechanism would be an intriguing material to study by a combination of hole-burning and photon-echo measurements.

The constant hole-burning efficiency for the photon-gated photochemical hole-burning process in Fig. 7(a) provides for holes that may be burned in 2.0 second burn times (and presumably much shorter time scales<sup>10</sup>) over a wide range of temperatures. The decreasing photophysical or one-color hole-burning efficiency with temperature means that the gating ratio and nondestructive reading of the two-color holes is improved by raising the temperature into the liquid nitrogen temperature range (77 K). The irreversibility of the photon-gated photochemical hole-burning process in TZT/ $\text{CHCl}_3$ /PMMA and the small amount of bleaching by the gating beam at 514.5 nm required that new samples be made after several holes were burned in one sample, which resulted in large sample-to-sample scatter in some of the data. One way to improve this situation would be to find a photon-gated hole-burning system in a glass with the possibility of reversibly erasing the holes with a third color. A reversible photon-gated hole-burning system would allow for temperature dependent gated hole-burning studies over a wide temperature range in a single glass sample without the associated sample-to-sample variations. Another way to improve sample-to-sample repeatability would be to utilize chlorinated host polymers, thus fixing the acceptor concentration. In recent measurements, photon-gated hole-burning for TZT in poly(vinyl chloride) has been observed<sup>9</sup>.

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## Figure Captions

**Figure 1.** One- and two-color persistent spectral holes burnt at 1.55 K into the  $S_1 \leftarrow S_0$  electronic absorption of TZT in  $\text{CHCl}_3/\text{PMMA}$ . Ratios of final to initial laser transmission spectra centered at 625.223 nm are shown at various times after (a) a two-color and (c) an additional one-color persistent spectral hole are burnt. (The spectrum labeled (a) is on scale and subsequent spectra are offset by multiples of -0.1). The two-color hole in (a) is burned in 2 seconds and the one color hole in (c) requires a much longer burn time of 200 seconds (the write intensity for both holes is  $3.7 \mu\text{W}/\text{cm}^2$  and the second 514.5 nm gating intensity is  $0.5 \text{ W}/\text{cm}^2$ ). The spectra are obtained at times  $(t_1, t_2)$  after the (one-color, two-color) holes are burnt of (a) (-, 10 s); (b) (-, 395 s); (c) (60 s, 730 s); (d) (300 s, 970 s); (e) (845 s, 1515 s); and (f) (3480 s, 4150 s). Note that the photochemical two-color hole does not decay appreciably whereas the photophysical one-color hole decays by half.

**Figure 2.** One- and two- color persistent spectral hole area decay at 1.55 K. The integrated areas of the (a) two-color and (b) one-color persistent spectral holes in Fig. 1 are plotted against  $\log(\text{time})$  as measured from the end of each burn. On the time scale shown the one-color hole depth decays linearly vs  $\log(t)$ . The two-color hole area is approximately constant in time.

**Figure 3.** One- and two-color persistent spectral holes burnt at 20 K. Reference and hole-burned monochromator transmission traces are shown in the upper portion and the corresponding fractional changes in absorption coefficient are shown in the lower portion of the figure. The noise in the fractional change in  $\alpha$  increases as  $\alpha$  goes to zero at longer wavelength. (a) a two-color hole is burned in 2 seconds at 632.029 nm. (b) the one-color hole burned at 624.947 nm requires a much longer burn time of 4380 s to achieve only a

fraction of the two-color hole depth burned in 2 s. (The write intensity for both holes is 7 mW/cm<sup>2</sup> and the gating intensity at 514.5 nm is 0.5 W/cm<sup>2</sup>).

**Figure 4.** One- and two-color hole depth and width growth curves at 2.03 K and 16.2 K. The hole depth and corresponding width curves are labeled by the same letter. (a) and (b) correspond to 2.03 K, and the broader, more slowly grown holes in (c) and (d) correspond to 16.2 K. (a) a write beam intensity of 14  $\mu$ W/cm<sup>2</sup> burns a one-color hole at 2.03 K on a 1000 second time scale. (b) including a gating intensity of 0.5 W/cm<sup>2</sup> at 514.5 nm produces a two-color hole in 1/100 the time needed in (a). (c) a two-color hole burned at a higher temperature of 16.2 K is broader and grows more slowly than at 2.03 K (in (c) the write intensity is doubled to 28  $\mu$ W/cm<sup>2</sup>). (d) a one-color hole burned at 16.2 K burns so slowly that a 100 times higher write intensity of 2.9 mW/cm<sup>2</sup> is needed to produce this growth curve. Comparing the hole widths in (c) and (d) also shows that using a higher write beam intensity broadens the hole.

**Figure 5.** Two-color hole width power broadening at several temperatures. At a given temperature, a burn fluence is selected at low power so that the hole depth is fixed between 0.05 and 0.10. The write beam intensity and burn time are reciprocally varied to hold the write beam burn fluence fixed, and the hole width is measured (with gating intensity at 514.5 nm held fixed at 0.5 W/cm<sup>2</sup>). The data are fit with a function described in the text to find the saturation intensity at each temperature of (a) 17  $\mu$ W/cm<sup>2</sup> at 6.4 K (write fluence = 0.23 mJ/cm<sup>2</sup>), (b) 1.5 mW/cm<sup>2</sup> at 8.4 K (write fluence = 1.7 mJ/cm<sup>2</sup>), (c) 2.5 mW/cm<sup>2</sup> at 23.6 K (write fluence = 4.3 mJ/cm<sup>2</sup>), and (d) 3.3 mW/cm<sup>2</sup> at 42.1 K (write fluence = 8.6 mJ/cm<sup>2</sup>).

**Figure 6.** Two-color hole-width variation with temperature. The widths of shallow two-color holes burned to a depth between 0.01 and 0.10 at intensities below the saturation intensity

are plotted over two decades in temperature. The data are fit by a constant plus power law function giving a low temperature limiting hole width of  $0.035 \pm 0.006 \text{ cm}^{-1}$ , a power of  $2.17 \pm 0.07$ , and coefficient of  $0.006 \pm 0.001 \text{ cm}^{-1} / \text{K}^{2.17}$

**Figure 7.** Variation of two- and one-color hole-burning efficiency with temperature. A quantity  $\eta^*$ , which is defined in the text and is directly proportional to the quantum efficiency for hole burning, is plotted with temperature for one- and two-color persistent holes. (a) the two-color hole-burning efficiency is roughly constant over two decades in temperature. By contrast, the one-color hole-burning efficiency in (b) is two orders of magnitude lower than the gated hole-burning efficiency at low temperatures and decreases to four orders of magnitude below the gated hole-burning efficiency at 100 K.















